National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2682b

Sulfur and Mercury in Coal

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the determination of sulfur, mercury, ash content, and calorific value ($MJ \cdot kg^{-1}$) in coal and materials of a similar matrix. SRM 2682b consists of 50 g of subbituminous coal ground to pass a 250 µm (60 mesh) sieve, homogenized, and packaged in an amber glass bottle.

Certified Values: The certified values for sulfur and mercury, expressed as mass fractions [1] on a dry basis, are provided in Table 1. The certified values are based on single NIST primary methods. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST.

Reference Values: The reference values for ash content [2] and calorific value are provided in Table 2. These reference values are based on data from laboratories participating in an interlaboratory study done in conjunction with the Canada Centre for Mineral and Energy Technology (CANMET) Service Program for the Evaluation of Codes and Standards (CANSPECS) in February 1998 (CANSPECS No. 55). Reference values are noncertified values that are the best estimates of the true values; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision and may not include all sources of uncertainty.

Information Values: Information values for selected elements, expressed as mass fractions on a dry basis, are provided in Table 3. These are noncertified values with no uncertainty assessed that are provided for information purposes only. In addition, data from the CANMET CANSPECS 55 Coal Round Robin are provided in the addendum to this certificate to demonstrate user experience with this material using conventional methods and to more fully characterize the matrix. The CANMET CANSPECS results were not used in calculating the certified values for sulfur and mercury and should **NOT** be used as substitutes for NIST values.

Expiration of Certification: The certification of SRM 2682b is valid, within the measurement uncertainties specified, until **31 December 2010**, provided the SRM is handled in accordance with the instructions given in this certificate (see Instructions for Use). This certification is nullified if the SRM is contaminated or otherwise modified.

Maintenance of SRM Certification: NIST will monitor representative samples of this SRM over the period of its certification. If substantive changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

The coordination of the technical measurements leading to certification was performed by G.C. Turk and M.R. Winchester of the NIST Analytical Chemistry Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald.

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Certification analyses for sulfur were performed by W.R. Kelly and K.E. Murphy of the NIST Analytical Chemistry Division. Certification analyses for mercury were performed by S.E. Long and W.R. Kelly of the NIST Analytical Chemistry Division. Moisture analyses were preformed by J.L. Mann and W.R. Kelly of the NIST Analytical Chemistry Division.

Homogeneity testing of the bulk material by X-ray fluorescence was performed by A.F. Marlow and P.A. Pella of the NIST Analytical Chemistry Division. The comparative sulfur analysis and bottle-to-bottle homogeneity testing was performed at the Electric Fuels Corporation Central Laboratory under the direction of the NIST Analytical Chemistry and Statistical Engineering Divisions.

Statistical analyses leading to certified and reference values were performed by W.F. Guthrie of the NIST Statistical Engineering Division.

INSTRUCTIONS FOR USE

Sampling: The unit should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 250 mg should be used for analytical determinations to be related to the sulfur and mercury values provided. The calorific value and ash content were determined using a nominal sample mass of 1 g. The SRM should be stored in its original tightly sealed bottle away from sunlight and intense sources of radiation.

Drying: In order to relate measurements to the certified and reference values that are expressed on a dry mass basis, users should determine a drying correction at the time of each analysis. The correction is determined by oven drying a separate 1 g sample in a nitrogen atmosphere at 107 °C ± 3 °C to a constant mass [3] or equivalent technique. For the purposes of certification, NIST operationally defined constant mass as the average mass of the first occurring three to five consecutive masses, for which the absolute change in mass from one weighing to the next is less than the observed pooled standard deviation of the weighing of at least three gold wires included as controls, or the sample mass when the loss of mass reaches a slope of zero. During drying at NIST, the mass loss of SRM 2682b samples was observed to stabilize after approximately 3.25 hours. The average mass loss measured at NIST for SRM 2682b was 12.79 % (1 s = 2.49 %, n = 8).

At NIST a study was also conducted to quantify the difference between drying in air and nitrogen atmospheres for SRM 2682b. The average weight loss determined at NIST for SRM 2682b dried in a convection oven in air at 105 °C ± 1 °C for two hours was 12.03 % (1 s = 2.45 %, n =8).

PREPARATION, HOMOGENEITY, AND ANALYSIS[1]

Source and Preparation of Material: Approximately 900 kg of coal was obtained from the Amax Coal Company Belle Ayr Mine near Gillette in Campbell County, WY. This mine, which opened for production in 1973, is an open pit mine that produces subbituminous coal from the Wyodak-Anderson coal seam that is part of the Powder River Basin. The coal was oven dried prior to processing in accordance with procedures outlined in ASTM D 2013. At least 500 kg of the coal was reduced in size to -60 mesh and screened prior to blending. The -60 mesh coal was blended in a stainless steel cone blender (approximate capacity 0.85 m^3). Additional information on sampling and preparation can be obtained from the NBS Special Publication 260-84 Sampling, Materials Handling, Processing, and Packaging of NBS Sulfur in Coal Standard Reference Materials.

Portions of the bulk material had been used to make SRM 2682 and SRM 2682a. The remaining bulk material was divided using the spinning riffler technique into 50 g units and subsequently issued as SRM 2682b.

Homogeneity Testing: Homogeneity testing on the bulk material was done by X-ray fluorescence. Homogeneity testing for sulfur on 50 g bottled units was done using a combustion-infrared detection analyzer according to ASTM D 4239 [4] on 12 bottles from the SRM 2682b lot selected by stratified random sampling. The standard deviation of random bottle-to-bottle differences in sulfur mass fraction is estimated to be 0.054 % relative to the certified sulfur mass fraction with a range of 0 % to 1.06 % at the 95 % confidence level.

[1] Certain commercial equipment, instrumentation, or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Analysis: The certified value for sulfur, reported in Table 1 as a mass fraction [1] on a dry basis (see Instructions for Use), is based on measurements by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [5] of SRM 2682a. The material designated SRM 2682b is a portion of the same bulk material that was used to prepare SRM 2682a. The sulfur concentration of SRM 2682a and SRM 2682b lots were directly compared by combustion-infrared detection to verify uniformity between lots. The certified sulfur value for SRM 2682b is based on the ID-TIMS measurements of the 2682a lot, with an adjustment for the differences observed between lots and adjustment to report the certified value based on drying in a nitrogen atmosphere.

The certified value for mercury, reported in Table 1 as a mass fraction [1] on a dry basis (see Instructions for Use), is based on measurements by isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP- MS) [8].

Table 1. Certified Values (Dry basis) for SRM 2682b

Element	Mass Fraction		
Sulfur	0.4917 %	±	0.0079 %
Mercury	108.8 µg/kg	±	2.9 µg/kg

The uncertainty in the certified value for sulfur is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO Guide [6]. The quantity u_c represents, at the level of one standard deviation, the potential combined effects of the uncertainty due to combustion/infrared detection measurement variability, ID-TIMS measurement variability (the ID-TIMS measurement variability for SRM 2682a was recomputed in accordance to ISO Guidelines before being used in the calculation of the expanded uncertainty for SRM 2682b), and conversion of values to nitrogen drying basis. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. The value of the coverage factor, $k = 2.315$, is determined from the Student's t-distribution with 7.82 degrees of freedom and a confidence level of 95 %.

The uncertainty in the certified value for mercury is expressed as an expanded uncertainty, $U = ku$, calculated according to the methods in the ISO Guide [6]. The observed mercury variation was much greater than expected for the analytical technique used. Therefore, a prediction interval was used to account for the mercury variability in this material [7]. The quantity u_c represents, at the level of one standard deviation, the potential combined effects of the uncertainties due to measurement variability and mercury inhomogeneity. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. The value of the coverage factor, $k = 2.305$, is determined from the Student's t-distribution with 8.02 degrees of freedom and a confidence level of 95 %.

Reference Values and Uncertainties: The reference value for ash content is based on data obtained from 35 laboratories using method ASTM D 3174 [2] in the CANMET CANSPECS Coal 55 Round Robin. The reference value for the gross calorific value is based on data obtained from 46 laboratories using conventional calorific methods in the CANMET CANSPECS Coal 55 Round Robin.

Table 2. Reference Values (Dry basis) for SRM 2682

Ash Content	6.32 %	±	0.42 %
Gross Calorific Value	25.66 $MJ \cdot kg^{-1}$	±	0.39 $MJ \cdot kg^{-1}$
	(11 030 $Btu_{th} \cdot lb^{-1}$	±	167 $Btu_{th} \cdot lb^{-1}$)

The uncertainties in the reference values for ash content and gross calorific value are each expressed as expanded uncertainties, $U = ku_c$, calculated according to the methods in the ISO Guide [6]. Prediction intervals were used to account for variability in the ash content and gross calorific value of this material [7]. The quantity u_c represents, at the level of one standard deviation, the potential combined effects of within-laboratory measurement uncertainty, between-laboratory uncertainty, material inhomogeneity, and the uncertainty in the conversion of samples dried in air to a nitrogen drying basis. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. For ash content, the value of the coverage factor, $k = 2.04$, is determined from the Student's t-distribution with 31.31 degrees of freedom and a confidence level of 95 %. For gross calorific value, the value of the coverage factor, $k = 2.02$, is determined from the Student's t-distribution with 43.18 degrees of freedom and a confidence level of 95 %.

Supplemental Information: The SRM 2682b mass fraction values listed in Table 3 for the major and minor elements are provided as additional information on the matrix.

Table 3. Information Values for SRM 2682b

(Mean Mass Fraction (mg/kg) Unless Noted)

Element	Mean Mass Fraction	Element	Mean Mass Fraction
Aluminum	0.46 %	Lanthanum	5.2
Antimony	0.19	Magnesium	0.2 %
Arsenic	1.0	Manganese	26
Barium	382	Nitrogen	1.0 %
Boron	39	Potassium	0.01 %
Bromine	3.7	Rubidium	< 2
Calcium	1.1 %	Samarium	0.78
Carbon	66.6 %	Scandium	1.5
Cerium	10	Selenium	0.91
Cesium	< 0.1	Sodium	0.10 %
Chromium	15	Thorium	1.5
Cobalt	1.7	Titanium	0.05 %
Europium	0.17	Tungsten	1.8
Hafnium	0.60	Uranium	0.52
Hydrogen	4.3 %	Vanadium	15
Iron	0.24 %	Zinc	8.6

REFERENCES

[1] Taylor, B.N., "Guide for the Use of the International System of Units (SI)," NIST Special Publication 811, 1995 Ed., (April 1995).

[2] ASTM D 3174-93, "Test Method for Ash in the Analysis Sample of Coal and Coke from Coal," **05.05** ASTM Book of Standards, West Conshohocken, PA.

[3] ASTM D 5142-90, "Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures," **05.05** ASTM Book of Standards, West Conshohocken, PA.

[4] ASTM D 4239-94, "Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods," **05.05** ASTM Book of Standards, West Conshohocken, PA.

[5] Kelly, W.R., Paulsen, P.J., Murphy, K.E., Vocke, R.D., and Chen, L.-T., "Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry," Anal. Chem., **66**, p. 2505, (1994).

[6] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993); see also Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, U.S. Government Printing Office, Washington DC, (1994); available at http://physics.nist.gov/Pubs/.

[7] Hahn, G.J. and Meeker, W.Q., "Statistical Intervals: A Guide for Practitioners," John Wiley & Sons, Inc., NY, (1991).

[8] Christopher, S.J., Long, S.E., and Rearick, M.S., "Development of High Accuracy Vapor Generation ICP-MS and its Application to the Certification of Mercury in Standard Reference Materials," Anal. Chem., Submitted for Publication, (November 2000).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (30l) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.

Addendum

Standard Reference Material® 2682b

Sulfur and Mercury in Coal (Subbituminous)

CANSPECS 55 Coal Round Robin Results: SRM 2682b was included as an unknown in the February 1998 CANSPECS 55 Coal Round Robin. Summary statistics reported by CANSPECS are provided in the addendum to this certificate to demonstrate user experience with this material using conventional methods and to better characterize the matrix. The CANSPECS 55 Coal Round Robin results should **NOT** be used as substitutes for NIST values.

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Addendum Issue Date: 06 February 2001

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Summary of Analysis Reported by CANSPECS

CANSPECS 55 Coal Sample NIST SRM 2682b

Parameter	Consensus Value	ASTM Method Referenced for Reproducibility and Repeatability	ASTM Reproducibility Standard Deviation	CANSPECS Reproducibility Standard Deviation	ASTM Repeatability Standard Deviation	CANSPECS Repeatability Standard Deviation	Number of Labs	Number of Methods
Moisture wt %	16.03	ASTM D 3173	0.18	0.60	0.11	0.12	79	22
Ash wt % db	6.21	ASTM D 3174	0.18	0.22	0.11	0.06	77	22
Volatiles wt % db	46.54	ASTM D 3175	0.35	1.47	0.18	0.27	63	17
BTU/lb db	10997	ASTM D 5865	44	95	18	18	71	16
Carbon wt % db	66.58	ASTM D 5373	0.89	0.50	0.23	0.22	31	14
Hydrogen wt % db	4.29	ASTM D 5373	0.11	0.24	0.06	0.06	31	13
Nitrogen wt % db	0.99	ASTM D 5373	0.06	0.07	0.04	0.02	32	13
Sulfur wt % db	0.48	ASTM D 4239c	0.03	0.03	0.02	0.01	77	18
Pyritic Sulfur wt % db	0.01	ASTM D 2492	0.05	0.01	0.03	0.00	14	4
Sulfate Sulfur wt % db	0.09	ASTM D 2492	0.01	0.01	0.01	0.01	14	3
Chlorine µg/g db	76	ASTM D 4208	77	102	21	6	22	10
Fluorine µg/g db	58	ASTM D 3761	5	12	5	3	10	6
Mercury ng/g db	85	ASTM D 3684	11	14	7	8	14	8
Selenium µg/g db	0.95	ASTM D 4606	0.14	0.06	0.10	0.11	9	7
Free Swelling Index (FSI)	0.0	ASTM D 720	0.7	0.0	0.4	0.0	27	4